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Energy shifts of *L*-levels in some 5th period elements due to oxidation and alloying

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With 7 figures in the text

ABSTRACT

The effect of oxidation and alloying on *L*-levels in cadmium and tin has been studied by means of the photo electron method. The L_{I} and L_{III} energies of Cd are shown to be lower by 0.8 and 0.6 eV respectively in the oxide than in the pure metal. Conversely, in the tin oxides SnO and SnO_2 the Sn *L* energies are found to be around 1 eV higher than in the metal. No shift is observed in the SnAu alloy. Infinitely thick as well as thin converters have been used.

Introduction

It has long been known that the wavelengths of X-ray emission lines and absorption edges depend to a certain extent on the chemical state of the emitting or absorbing element. Generally, the effect of putting an element into a compound or an alloy is small for transitions between inner levels and more pronounced for emission bands and absorption edges. Consequently, it has very often been stated that the inner electron levels are shifted less than the outer ones. However, before making such a statement, it should be specified to which level the energies are referred.

Recently a new method has been developed for studying the effect of chemical binding and alloying on inner electron levels. This method, which is described in ref. [1], is based on a precise energy analysis of photo electrons expelled from an inner shell by x-radiation. It can be shown that the energy shift observed for the photo electrons on going from the pure element to a chemical compound or an alloy is equal to the energy shift of the level in question with respect to the Fermi level. In ref. [1] it was found that for copper in metallic form and in oxide (CuO) the shift was greatest for the *K* shell electrons (4.4 eV), contrary to the statement above. The aim of the present investigation was to look for similar effects in the *L* shells of some 5th period elements, using the photo electron method, and also to demonstrate the possibility of making thick converting layers rather than thin evaporated films.

The photo electron sources

The same apparatus as in ref. [1] was used for this investigation. It consists of a double-focussing β-spectrometer without iron for the energy analysis of the photo electrons. An x-ray tube is lowered into the spectrometer tank, and the reference material and its compound or alloy are successively slid into the x-ray beam. It was shown in ref. [1] that it is possible to move different parts of the source holder, with different converter materials deposited on it, into the beam without seriously changing the calibration constant of the spectrometer. The small shifts actually observed between the photo lines from the same converter material deposited on different parts of the *linear* source backing can easily be corrected for: the converter frame is made in *three* sections with the same material on the two outer sections. If, because of a slightly different position of the two samples when slid into the x-ray beam, the photo lines from these parts are shifted, the proper reference value for the middle section can be obtained by linear interpolation.

Thin layers of the converter materials were prepared by evaporation onto an aluminum backing, 15 μ thick and approximately 1 mm wide, the thickness of the films being of the order of 100 Å. In general one really has to avoid thick converters, since for a thick sample those photo electrons which have been scattered inelastically in the source will predominate over those penetrating the converter without suffering any energy loss. This might completely change the shape of the photo line and prevent an accurate energy determination. Fortunately, however, very few electrons are scattered with an energy loss smaller than approximately 15 eV, the mechanism being such as to make the electrons tend to give up their energy in discrete amounts [2, 3]. Thus, the spectrum of electrons which have suffered energy losses consists of a series of discrete peaks. These are in many cases superimposed on a continuous background. Hence, if thin sources are used, and if the resolution of the spectrometer is sufficiently good, it is possible to separate the peak of the undisturbed electrons from the first characteristic energy loss peak.

For the elements of the fifth period it turns out that with the apparatus used in this investigation, it is also possible to use *thick* sources for a study of the L_{III} photo electrons expelled by copper $K\alpha$ radiation. The resolution of the spectrometer can easily be set to give a line width for the Sn L_{III} (Cu $K\alpha_1$) line, of about 8 eV, including the contribution from the natural widths of the copper $K\alpha_1$ radiation and the L_{III} level of tin. Moreover, the intensity of the inelastically scattered electrons does not increase significantly in the energy region close to the main peak when the converters are made thick. This opens up quite new possibilities for the source preparation. As fas as metals are concerned the technique of evaporating thin films is only limited by the temperature of evaporation, but when there is a need for sources with a more complex composition the evaporation technique often meets with great difficulties, and special methods have to be resorted to. Now, if there is no longer a demand for *thin* sources and the conductivity of the material is sufficiently high to prevent charging up effects, i. e. if one is concerned with conductors or semiconductors, bulk sources may easily be prepared [4]. In fig. 1 is shown a source holder with thick converters of Sn and SnO. The aluminum *strip* is now changed for an aluminum *bar* in which a groove, 0.6 mm wide, has been made. The middle section contains a piece of metallic Sn which fits into the groove, while the outer sections are filled with a powder of SnO. It

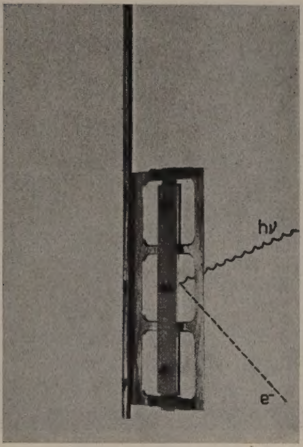

Fig. 1. Source holder for thick converters. The samples are pressed into the groove of the aluminum bar either as a powder or as small metal slabs. Here the two outer sections contain a powder of SnO with metallic tin in the middle section. Sketched in the figure are the incoming x-radiation and the expelled photo electrons.

is true that SnO itself is a semiconductor but one still has to make sure that the small grains of the substance get in electrical contact with each other, so, in order to obtain a sufficiently high conductivity the oxide was mixed with graphite powder. When thin sources are used the easiest way to mount them is in such a way as to let the x-radiation penetrate the backing as well as the source itself. This is obviously not the proper geometry for thick layer sources, in which case the same surface should be irradiated as that from which the photo electrons are ejected into the spectrometer. This is indicated in Fig. 1.

Experimental results

The demand for the samples to be conductors or semiconductors limits the number of compounds that can be chosen. In the present investigation the L-level shifts of the fifth-period constituent were studied in the following compounds and alloys: CdO, SnO, SnO_2 and SnAu.

Cd–CdO

Cadmium oxide is probably an excess semiconductor [5]. Resistivity measurements at temperatures above 150°C yield an activation energy of 0.4 eV [6]. Thin "transmission" sources as well as thick "reflexion" sources were prepared. The technique of oxidizing the Cd films was the same as that of ref. [1], namely heating the evaporated metal layers in air at 200°C over a period of about 12 hours. Diffraction patterns were taken of metallic as well as of oxidized samples, made simultaneously with and treated in the same way as those used for the shift measurements. This was done in order to check the composition of the "transmission" samples. In Fig. 2 are shown two diffraction patterns, one from a thin metallic Cd film and the other one from a film that was oxidized under the conditions above; Cd crystallizes in a hexagonal structure with $a_0 = 2.9793$ Å, $c_0 = 4.6181$ Å, whereas CdO has a face-centered cubic lattice of NaCl type with $a_0 = 4.6953$ Å

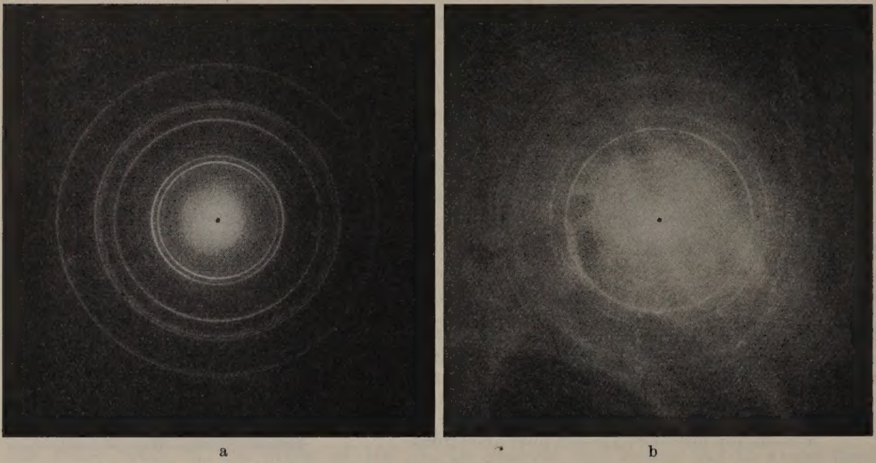

Fig. 2. Electron diffraction patterns of (*a*) metallic Cd and (*b*) the oxide CdO.

[7]. All of the rings in the Cd pattern could be indentified with reflexes from metallic cadmium. In the oxide pattern all reflexes originated in CdO except for two very weak rings, which could be attributed to the Cd structure only; hence the oxidation was almost complete.

In the cadmium oxide the L_{I} and L_{III} energy shifts were measured, two determinations being made of the L_{I}- and three of the L_{III}-shifts. Copper $K\alpha_1$ radiation was used for the production of photo electrons throughout all measurements in this investigation. Table 1 gives the shifts observed in the different recordings as well as the type of converter used in each case (transmission or reflexion).

The minus sign of the shifts indicates that the electron binding energies are *smaller* in the oxide than in the metal. The errors are set to be somewhat larger than the reproducibility, since only a small number of runs were made. Typical results obtained from the shift measurements of the two shells are shown in Fig. 3.

Table 1. Cd–CdO.

L_{I}		L_{III}	
Shift (eV)	Type of converter	Shift (eV)	Type of converter
−0.8	transm.	−0.4	transm.
−0.8	transm.	−0.6	refl.
		−0.7	transm.
Mean value −0.8 ± 0.3		Mean value −0.6 ± 0.3	

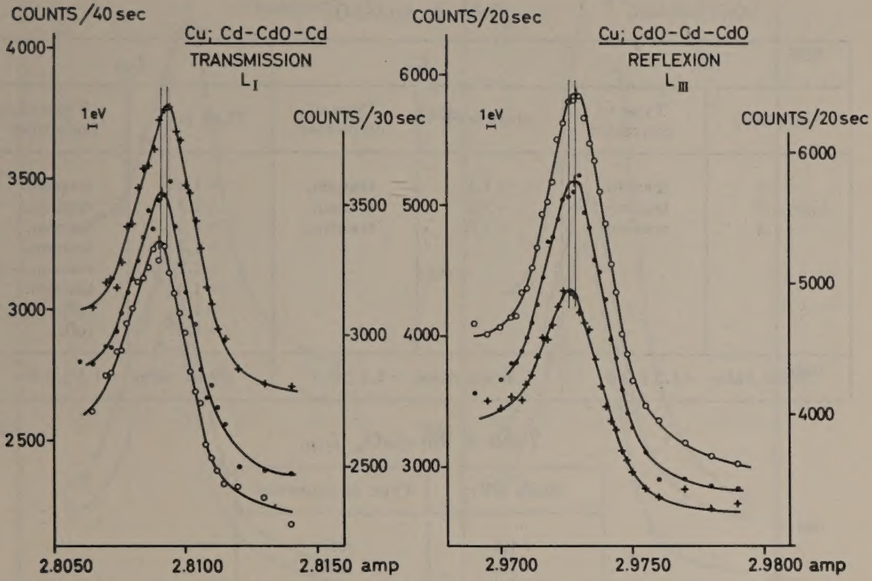

Fig. 3. L_{I} and L_{III} photo lines from metallic Cd and from CdO. The L_{I} lines were obtained from a thin source with the metal in the outer sections (open and filled circles, right ordinate axis) and the oxide in the middle section (crosses, left ordinate axis). The L_{III} photo lines were obtained from thick reflexion type converters with metallic Cd in the middle section (crosses, right ordinate axis) and CdO in the outer sections (open and filled circles, left ordinate axis). Copper $K\alpha_1$ radiation was used for the production of photo electrons.

Sn–SnO

Both tin oxides are semiconductors [5], SnO being of the deficit type and SnO_2 an excess semiconductor. The finite resistivity of SnO is thought to be due to deviations from a perfect stoichiometric composition of the oxide [5]. Transmission and reflexion type converters of this oxide were prepared in the same way as for CdO. Three measurements were made of the L_{I} and L_{II} shifts in SnO, and the L_{III} shift was measured eight times. The results are given in Table 2.

Here the effect of oxidation is such as to *increase* the L binding energies contrary to the case of cadmium. This can also be seen in Fig. 4, in which are shown the L_{I}, L_{II} and L_{III} photo electron lines from tin in metallic form and in the 2^+ state of oxidation. To make possible a direct comparison of the same photo-lines from a thin transmission type converter and a thick reflexion type, two examples are given for the L_{III}-shift, one for each type of converter. The composition of the transmission samples was again checked with electron diffraction (Fig. 5). Metallic Sn has a tetragonal structure with $a_0 = 5.831$ Å and $b_0 = 3.182$ Å [7], and the oxide SnO also has tetragonal structure with cell constants $a_0 = 3.77$ Å, $c_0 = 4.77$ Å. On analyzing the diffraction patterns it was found that they were both free from rings due to reflexions from extraneous structures.

Table 2. Sn–SnO.

L_I		L_{II}		L_{III}	
Shift (eV)	Type of converter	Shift (eV)	Type of converter	Shift (eV)	Type of converter
+1.0	transm.	+1.1	transm.	+1.2	transm.
+1.5	transm.	+1.2	transm.	+1.2	transm.
+1.4	transm.	+1.0	transm.	+1.5	transm.
				+1.3	transm.
				+1.3	transm.
				+1.5	transm.
				+1.1	refl.
				+1.5	refl.
Mean value +1.3±0.3		Mean value +1.1±0.3		Mean value +1.3±0.2	

Table 3. Sn–SnO_2, L_{III}.

Shift (eV)	Type of converter
+1.3	refl.
+1.0	refl.
+1.1	refl.
Mean value +1.1±0.3	

Sn–SnO_2

The L_{III} binding energy of Sn in its highest state of oxidation was measured in three samples, all being of the reflexion type. Here, as well as for the other oxides, the metallic reference converter was in some cases put in the middle section, and for other samples it was put in the two outer sections in order to give a check on the linearity of the sources. The oxide was known by chemical analysis to contain less than 0.3 % impurities.

Table 3 gives the shifts obtained from the three measurements made of the Sn L_{III} energy in Sn and SnO_2, and in Fig. 6 is shown the result obtained from one of the samples. The L_{III} shift is the same for this oxide as for SnO within experimental errors.

Sn–SnAu

It was also thought to be of interest to look for effects of *alloying* on the binding energies. In the case of an alloy it is most advantageous to have thick converters, since the techniques of evaporating or electroplating alloys without changing

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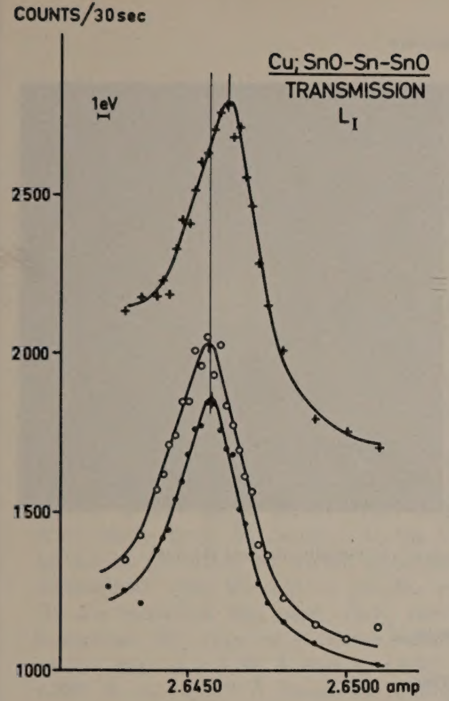
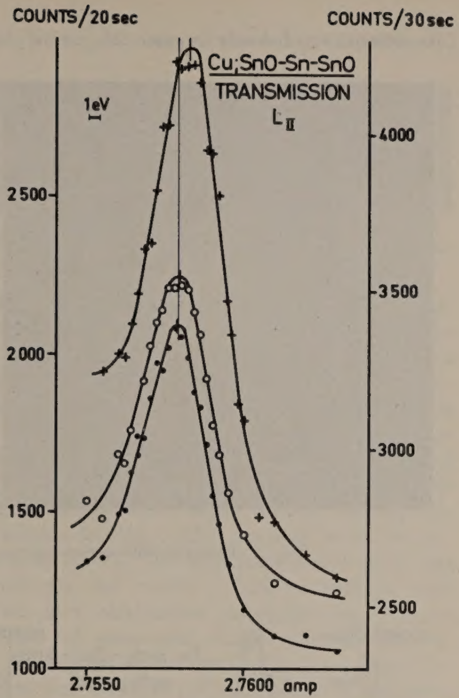
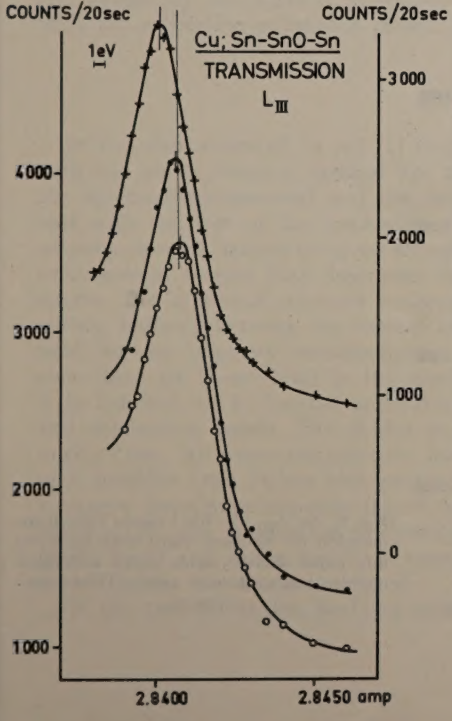
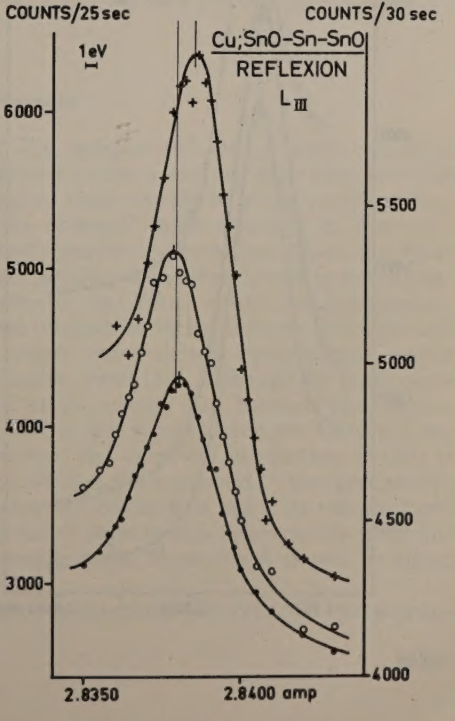
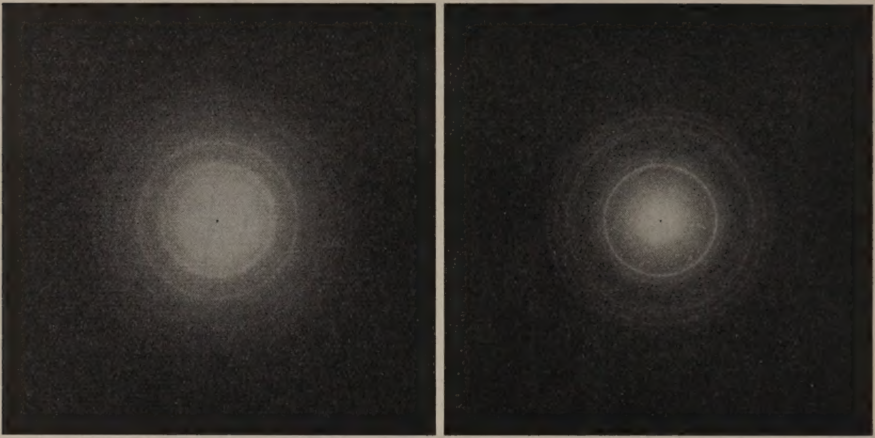
Fig. 4. Photo electron lines from the three *L* subshells of tin in metallic form and in the oxide SnO. The type of converter (transmission or reflexion) and the substance held in each section of the source holder are indicated. When two ordinate axes are given, the one to the right pertains to the curve plotted with crosses. The interpolated position of a "zero shift" line from the middle section of the source is marked with a vertical line equidistant from the peaks of the photo lines from the two outer sections. Two examples are given of the L_{III} photo lines, one for each type of converter.


COUNTS/30 sec
Cu; SnO-Sn-SnO
TRANSMISSION
L_I
1eV
2500
2000
1500
1000
2.6450
2.6500 amp


COUNTS/20 sec
COUNTS/30 sec
Cu;SnO-Sn-SnO
TRANSMISSION
L_{II}
1eV
2500
2000
1500
1000
4000
3500
3000
2500
2.7550
2.7600 amp


COUNTS/20 sec
COUNTS/20 sec
Cu; Sn-SnO-Sn
TRANSMISSION
L_{III}
1eV
4000
3000
2000
1000
3000
2000
1000
0
2.8400
2.8450 amp


COUNTS/25 sec
COUNTS/30 sec
Cu;SnO-Sn-SnO
REFLEXION
L_{III}
1eV
6000
5000
4000
3000
5500
5000
4500
4000
2.8350
2.8400 amp



a

b

Fig. 5. Electron diffraction patterns of (*a*) metallic Sn and (*b*) SnO.

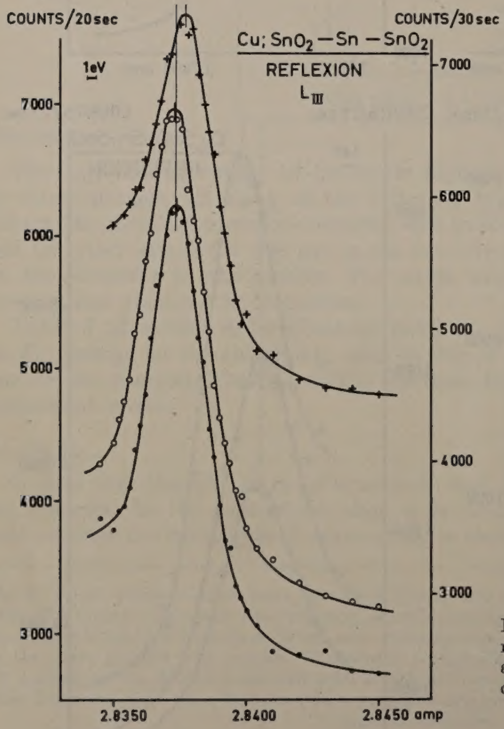


Fig. 6. Sn L_{III} (Cu $K\alpha_1$) photo lines from metallic Sn (crosses, right ordinate axis) and from stannic oxide (open and filled circles, left ordinate axis). Thick converters.

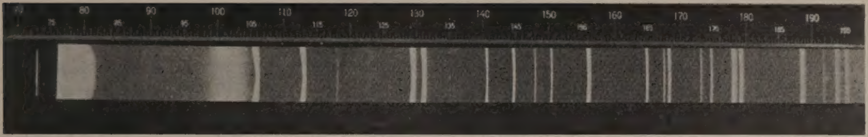


Fig. 7. Powder diffraction pattern of the SnAu alloy taken with a Guinier camera and Cu $K\alpha$ radiation.

the composition are not too reliable. SnAu was chosen for the present investigation. It was of special interest to have tin as one of the constituents, since the effect of oxidation of tin had also been studied, giving energy shifts of the order of one electron volt (Tables 2 and 3). The tin-gold system has several stable phases, SnAu being the only one where all tin atoms have gold atoms as nearest neighbours in the lattice. This alloy melts at 418°C and was prepared by heating a mixture of 50 at.% Sn and 50 at.% Au in an evacuated pyrex tube to well above the melting point. The alloy could easily be machined into small rectangular slabs fitting the groove of the source holder. Two measurements were made of the Sn L_{III} (Cu $K\alpha_1$) photo lines. In contrast to the findings for the oxides, no shift could be observed in the alloy to within experimental errors. The structure of the alloy was determined with the aid of powder patterns, for which a Guinier camera with Cu $K\alpha$ radiation was used. CaF_2 served as a calibration substance. SnAu has a hexagonal $B8_1$ type of structure, and the cell constants obtained in this investigation were $a_0 = 4.32$ Å and $c_0 = 5.52$ Å, in good agreement with the values $a_0 = 4.323$ Å, $c_0 = 5.523$ Å found by Stenbeck and Westgren [8] and those of Batterna and Jaeger [9], $a_0 = 4.316$ Å, $c_0 = 5.507$ Å. Fig. 7 shows a powder pattern of SnAu with no calibration substance present.

Comments

It was demonstrated in ref. [1] that the energies and energy shifts measured with the photo electron method are those relative to the common Fermi level of the spectrometer material and the sample, which should be put in electrical contact with the rest of the apparatus. The chemical shifts obtained in X-ray absorption spectra cannot be given an equally simple interpretation. There are, however, several factors that determine the position of the Fermi level in a semiconductor. For a perfect intrinsic semiconductor the Fermi level is located approximately halfway between the valence and conduction bands, whereas this does not hold for an impurity semiconductor, which under certain circumstances might even have its Fermi level in the conduction band [10], although in most cases it is believed to be located somewhere in the energy gap between the valence and conduction bands. The oxides studied in this investigation are all of the impurity type. At room temperature, however, the electrical conduction in CdO is of a metallic type. It has been proposed [6] that the excess Cd^{++} ions give rise to a narrow band approximately 0.4 eV below the conduction band. At temperatures below $\simeq 150^\circ$ the conduction preferably takes place in this incompletely filled impurity band and hence for these temperatures the Fermi level should lie about 0.4 eV below the conduction band.

Of the two tin oxides, SnO is a deficit semiconductor and SnO_2 an excess semiconductor. Determinations of the conductivity as a function of the absolute temperature have been made for the stannic oxide [11]. These measurements did not give an unambiguous value for the activation energy, but in the temperature region 200–300°K it was found to be approximately 0.05 eV. There seems to be no correlation for the elements studied in the present investigation between the sign of the energy shifts and the type of semiconductor (deficit or excess) of which the element is a constituent. As to the magnitude of the shifts, they are found, both for cadmium and tin, to be smaller than those of the L levels in copper [1]. Also, the L_{I} shifts are not significantly greater than the L_{II} and L_{III} shifts.

As can be seen in Figs 3, 4 and 6 the photo electron lines obtained from the reflexion type converters compete favourably with those from thin evaporated films, as signal to background intensities are concerned, and the lines are equally well resolved from the first discrete energy loss peak. A comparison between the photo line from a metallic converter and its oxide shows that the distortion of the low energy flank due to inelastically scattered electrons is even less for the oxide than for the metal.

It was found in ref. [1] that for Cu the widths of the L photo lines were a few tenths of an eV greater in the oxide; the same effects could be observed in the present investigation for the element tin. This broadening is always smaller than 0.5 eV, if the width of a photo line is defined as twice the width of the high energy flank at half maximum intensity.

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REFERENCES

1. NORDLING, C., SOKOLOWSKI, E., and SIEGBAHN, K., Ark. f. fysik *13*, 483 (1958).
2. PINES, D., Solid State Physics, 1; Editors: SEITZ, E., and TURNBULL, D. Academic Press Inc.
3. MARTON, L., LEDER, L. B., and MENDLOWITZ, H., Advances in Electronics and Electron Phys. *7*, 183 (1955).
4. SOKOLOWSKI, E., Ark. f. fysik *15*, 1 (1959).
5. MEYER, W., Zeitschr. f. Elektroch. *50*, 274 (1944).
6. HOGARTH, C. A., Proc. Phys. Soc. *64 B*, 691 (1951).
7. X-ray Diffraction Data, published by the American Society for Testing Materials.
8. STENBECK, S., and WESTGREN, A., Zeitschr. Phys. Chem. *B 14*, 91 (1931).
9. BATTERNA, J. A., and JAEGER, F. M., Proc. Acad. Amst. *35*, 916 (1932).
10. HUTNER, R. A., RITTNER, E. S. and DU PRÉ, F. K., Philips Research Repts. *5*, 188 (1950).
11. BAUER, G., Ann. d. Phys. *30*, 433 (1937).

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